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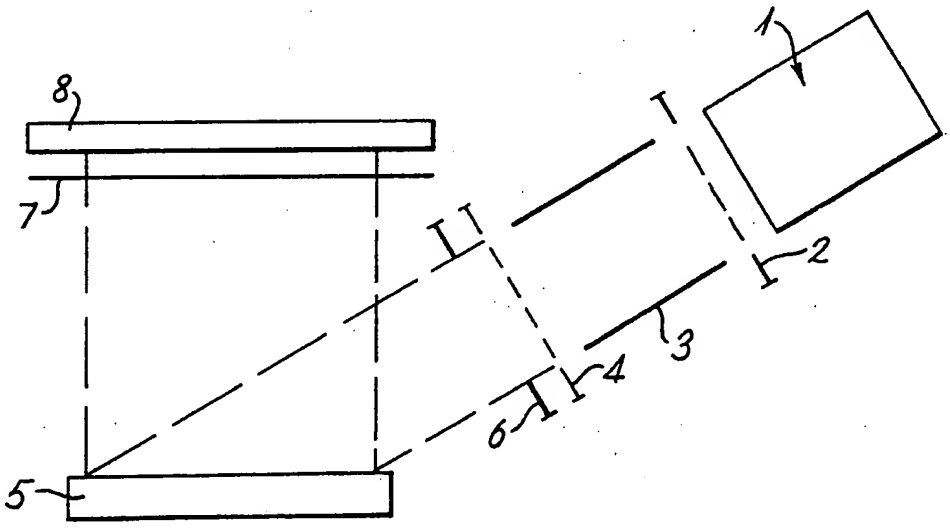

(57) Abstract

A method of manufacture of multilayer devices comprises successively directing charged particles at a body of a first material (5) thereby causing the separation of particles of material from said body, depositing said particles in atomic or molecular layers on a substrate (8) and then directing charged particles at a body of a second material, thereby causing separation of particles of said second material from said body of the second material and then depositing said particles of said second material in atomic or molecular layers on the layers of said first material on said substrate.

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MULTILAYERED STRUCTURES

This invention relates to multilayered structures and methods of fabrication thereof. It finds particular application in structures usable in electronic and optical devices. Such structures may be constructed on a flat or figured substrate and are characterised by a periodicity d which may vary in a predetermined manner throughout the thickness of a stack and/or laterally over the surface of the substrate.

According to the present invention there is provided a method of manufacture of multilayer devices comprising successively directing charged particles at a body of a first material, thereby causing the separation of particles of material from said body, depositing said particles in atomic or molecular layers on a substrate and then directing charged particles at a body of a second material, thereby causing separation of particles of said second material from said body of the second material and then depositing said particles of said second material in atomic or molecular layers on the layers of said first material on said substrate.

There is also provided a multilayer device comprising a substrate having a plurality of layers each of substantially uniform molecular thickness deposited thereon.

An embodiment of the invention will now be described by way of example, with reference to the accompanying drawings, in which:-

Figure 1 shows in section a simple multilayer structure with two different constituent layers

Figure 2 shows computed reflectivities and phase changes at an interface between carbon and platinum layers

Figure 3 shows the measured reflectivity spectrum of a Pt-C-Pt etalon

Figure 4 shows the reflectivity of a Pt-C multilayer structure

Figure 5 is the reflectivity of a different Pt-C multilayer structure and;

Figure 6 is the schematic arrangement of apparatus suitable for making multilayer structures in accordance with the invention.

Referring now to the drawings, a multilayer stack of periodicity d is made up of sublayers of thickness t_1, t_2 --- t_N. Figure 1 illustrates a simple example of a multilayer with a substrate S and alternate layers L1,L2 of two different materials. The periodicity d is given by

$$d = t_1 + t_2$$

where d is constant both laterally and throughout the stack.

Each sublayer may be crystalline (polycrystalline or single crystal) and may be epitaxial with its neighbours. Alternatively, some of the layers may be amorphous. The number of periods (which may not be integer) can range from that appropriate to a single film to thousands.

The crystalline/crystalline or crystalline/amorphous multilayers may be used as mirrors, filters and polarisers for electromagnetic radiation. At the short wavelength end of the spectrum mirrors, filters and polarisers can be made from existing crystalline material by utilising the Bragg's reflection condition

$$2d \sin\phi \left(1 - \frac{\bar{\delta} + i\bar{n}}{\sin^2\phi}\right) = p\lambda \qquad (1)$$

where

$$\bar{\delta} = \gamma\delta_1 + (1 - \gamma)\delta_2$$

$$\bar{n} = \gamma n_1 + (1 - \gamma)n_2$$

$$t_1 = \gamma d$$

and

$$t_2 = (1 - \gamma)d$$

and the complex refractive index of each layer is

$$n = (1 - \delta) - in$$

Equation (1) can be extended to cover any number of layers t_1, t_2 ---t_N in the period d.

The reflectivity at each interface of the stack is maximised when the density difference between the chosen pair of adjoining layers, A,B say, is maximised. This is accomplished by depositing A in the crystalline phase and B in the amorphous phase. This is illustrated in Figure 2 which shows the computed reflectivities and phase changes at a carbon-platinum interface. The reflectivities R_S, R_p (for linearly polarised light) are plotted for ρ_{carbon} = 2250K m^{-3} (the value for graphite) and $\rho_{amorphous}$ = 1800K m^{-3} (appropriate to amorphous carbon); the platinum is crystalline.

Figure 3 shows the measured reflectivity spectrum of a Pt-C-Pt etalon deposited on a silicon substrate. The amorphous carbon spacer thickness is 26.2nm.

With increasing number of layers the Bragg reflection peak develops as shown in Figure 4 for a 31/30 Pt-C multilayer (d = 3.7 nm) at wavelength λ = 0.834 nm. The higher order Bragg reflections (p = 2,3), equation (1), are also detected, as is shown in Figure 5.

The multilayer of Figure 4 exhibits the theoretical reflectivity. The platinum layers in this stack are only five

atoms thick, but are electrically continuous. With such thin crystalline films each layer has to be an integer number of atom layers thick in order to produce a commensurate stack.

If the substrate on which the multilayer is deposited is then perforated by a process such as chemical or sputter etching, a transmission filter is obtained. Alternatively, the transmission characteristics of the multilayer may be utilised by depositing the multilayer on a substrate which has little or no absorption at the wavelengths considered

Referring to Figure 2 it is seen that the reflectivity R_p falls to a low value at the 'pseudo Brewster angle'. A multilayer which has its first order Bragg reflection peak at this angle of incidence is then a very efficient linear reflection polariser.

Broad band reflectors, filters and polarisers are obtained if the spacing of the stack varies throughout the stack thickness. This produces a series of overlapping/adjoining Bragg reflection peaks on a wavelength scale at particular angles of incidence. Alternatively the spacing d may vary laterally. This will give broad band reflectivity from a flat substrate or allow point focussing of monochromatic radiation from a multilayer on a figured substrate.

The materials from which the multilayer is constructed are those appropriate to the wavelength range considered. The Pt-C multilayer used as the example will operate at those wavelengths where carbon is non-absorbing. In another embodiment, it may be replaced by an alternative material, such as silicon.

The Pt-Si multilayer illustrates another possibility. although deposited as metallic platinum - amorphous silicon, a reaction may occur between the platinum and silicon to form platinum silicide. The resulting multilayer is then a crystalline platinum silicide - amorphous silicon assembly. With further change in the deposition conditions the silicon can be made crystalline to give an epitaxial stack of platinum

silicide - silicon. With this assembly any diffuse scattering which may be associated with the polycrystalline-amorphous stack is reduced/eliminated but the density difference between adjoining layers is reduced and hence stack reflectivity. Similar epitaxial crystalline-crystalline stacks can be formed from Co-Si, Ni-Si and the other transition metal-Group IV elements.

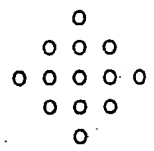
When deposited as a thin film, the electronic band structure of a crystalline solid is different from that of the bulk material. Examples are the transition metal dichalcogenides ($MoTe_2$ etc) where the band gap increases with decreasing thickness. This effect may be used to construct semiconductor devices with unique properties. Furthermore, lateral changes in the film thickness may be used to produce an anisotropic semiconductor.

Compositional changes in the crystalline/crystalline or crystalline/amorphous multilayer produce a 'superlattice' tructure. In the case of epitaxial multilayers (e.g. GaAs/GaAlAs) of specific periodicity the different energy gaps of the GaAs, GaAlAs occur periodically throughout the thickness of the stack.

Assemblies of thin films of Fe, Co, Ni etc. separated by carbon films (say) exhibit ferromagnetic resonance shift due to coupling between the separated thin (Fe) films of the stack.

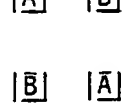
Apparatus suitable for fabricating multilayer devices in accordance with the invention is illustrated in Figure 6. This comprises an ion gun 1 to generate a flux of ionised particles. An aperture screen 2, an electric/magnetic field deflecting/collimating lens 3 and collimating apertures 4 direct the ion beam on to a target 5. Particles of the target material, which may be subsequently deflected electrically or magnetically are subsequently neutralised by an ion-beam neutraliser 6. They then pass through a substrate mask 7 and are deposited on to a substrate 8, on a temperature-controlled, rotatable work table 9.

The aperture screen 2 and collimating apertures 4 may alternatively consist of single rectangular apertures so that the whole of the target 5 is illuminated or a series of small apertures arranged in a specific pattern e.g.



These small apertures may be of equal area or of systematically changing area - in the latter case this gives a varying ion-beam flux on to the target 5 and hence a variable (lateral) d spacing.

Alternatively, the aperture pattern may match the compositional pattern of the target e.g.



so that a lateral displacement of the target or aperture screen results in material B being sputtered in addition/or instead of material A. This is useful for compositional changes. If the multilayer consists of two materials A and B, then it is sufficient to replace the target of material A by a target of material B.

An approximately sinusoidal density variation throughout the stack is obtained by oscillating the target between materials A and B to give a varying alloy composition (hence electron density) Layers with this sinusoidal variation only gives first order Bragg reflection. (Fourier transform)

In a preferred method, two materials A,B (e.g. Pt-Si) are deposited to give a conventional multilayer Pt/Si of polycrystalline Pt and amorphous Si. Heat treating the sample converts to a Pt-Pt_2Si-PtSi-Pt2Si-Si which, to a first approximation is a stepped sinusoid; diffusion at the interface will give the graded density variation

This can be further improved by using Ni-Si, say, which has the compound forms Ni_2Si, NiSi, $NiSi_2$. This gives a stepped layer sequence Ni-Ni_2Si-NiSi-$NiSi_2$-NiSi-Ni_2Si-Ni. The relative thicknesses of Si and Ni are chosen to allow the formation of some or all of these compounds

Other possible material (M) combinations (with Si) are:

For M_2Si Ni_2Si, Pd_2Si, Pt_2Si, Co_2Si

For MSi PtSi, PdSi, NiSi, CoSi, FeSi, RhSi, HfSi, TiSi, MnSi.

For MSi_2 $TiSi_2$, $ZrSi_2$, $HfSi_2$, VSi_2, $NbSi_2$, $TaSi_2$, $CrSi_2$, $MoSi_2$, WSi_2, $NiSi_2$, $CoSi_2$, $FeSi_2$, $MnSi_2$.

Germanium may be substituted for silicon in certain applications.

Mask 7 defines the lateral dimensions of the multilayer or may be used to introduce a periodic lateral variation in d.

The temperature of the substrate can be varied over a wide range from below to above room temperature in order to minimise adsorption atom mobility or accelerate reaction between deposited species.

The ion beam neutraliser 6 is to eliminate charging of the target and subsequent ion beam wandering. The electric/magnetic field collimator 3 may also be used to vary the flux distribution incident on the aperture screen 4.

The mechanics of diffusion must be considered in setting up the M-Si thickness combination. In the formation of M_2Si the

metal atom is the dominant diffusing species; in MSi and in the formation of MSi_2 the Si atom is dominant diffusing species.

The density profile is also influenced by solubility. Thus in the reaction of Ni and V with Si there is no noticeable solution of Si in these metals prior to silicide formation. In the case of Fe, however, Si dissolves in the Fe film up to 25% (at 400°C) before the formation of FeSi.

Monolayers (reflecting mainly at one order) produced by the above method, when deposited on the appropriate grating substrate, will produce a 'blazed' grating.

In an alternative embodiment, a multiple gun sputtering system may be used in place of the single gun system above.

CLAIMS

1. A method of manufacture of multilayer devices characterised in that it comprises successively directing charged particles at a body of a first material, thereby causing the separation of particles of material from said body, depositing said particles in atomic or molecular layers on a substrate and then directing charged particles at a body of a second material, thereby causing separation of particles of said second material from said body of the second material and then depositing said particles of said second material in atomic or molecular layers on the layers of said first material on said substrate.

2. A method of manufacture of multilayer devices as claimed in claim 1 characterised in that it includes the step of forming a crystalline layer on said substrate.

3. A method of manufacture of multilayer devices as claimed in claim 2 characterised in that the step of forming a crystalline layer on said substrate comprises heat treating at least one of the layers of said first and second materials.

4. A method of manufacture of multilayer devices as claimed in either claim 2 or claim 3 characterised in that the crystalline layer comprises a compound of the components of said first and said second material.

5. A method of manufacture of multilayer devices as claimed in any one of the preceding claims characterised in that it includes a heat treatment process to cause diffusion of material between at least some of said layers.

6. A method of manufacture of multilayer devices as claimed in any one of the preceding claims characterised in that the flux of said charge particles is modified to cause a lateral variation of the composition of at least one of said layers on said substrate.

7. A multilayer device characterised in that it comprises a substrate having a plurality of layers each of substantially uniform molecular thickness deposited thereon.

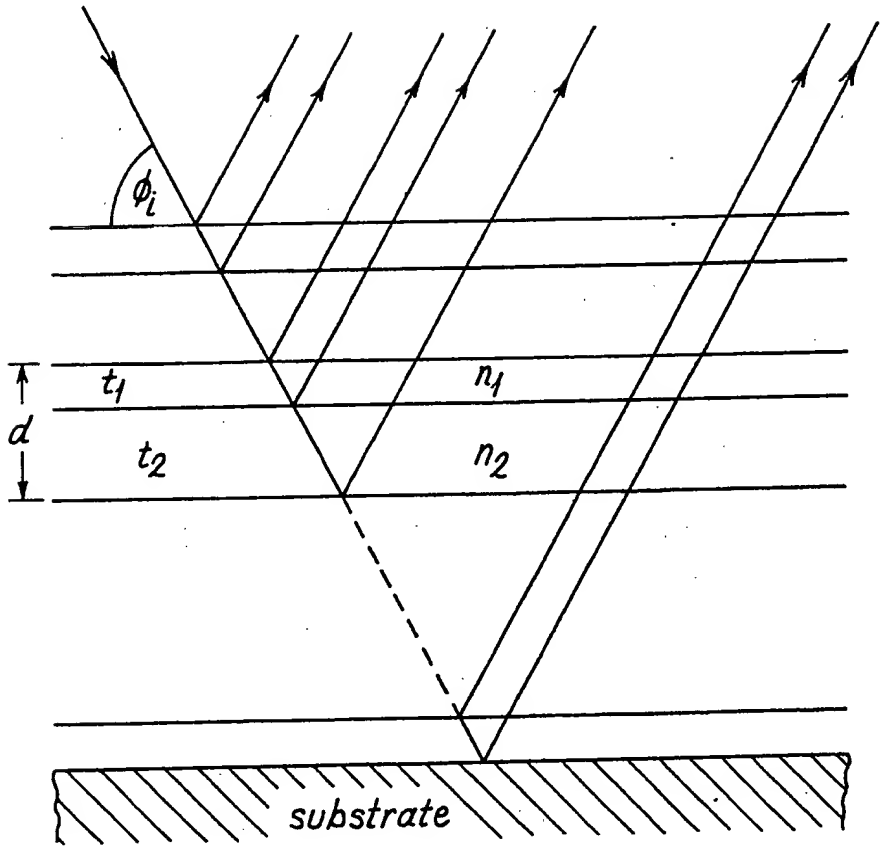
8. A multilayer device as claimed in claim 7 characterised in that at least one of said layers is crystalline in structure.

9. A multilayer device as claimed in claim 8 characterised in that at least one of said layers is amorphous in structure.

10. A multilayer device as claimed in claim 9 characterised in that it includes a plurality of alternating crystalline and amorphous layers.

11. A multilayer device as claimed in claim 8 characterised in that it includes at least one intermediate layer which includes a compound of at least one of the components of each of the two contiguous layers.

12. Apparatus for fabricating multilayer devices in accordance with the method of claim 1 characterised in that it comprises particle generating means (1) to generate a flux of ionised particles, filter means (2) to screen the flow of said particles, deflecting means (3,4) to direct the ionised particles on to target means (5) to displace particles of charge material therefrom, deflection means to direct said particles towards a substrate and neutraliser means (6) to neautralise the charge of said particles.



$$r_s = \frac{n_1 \sin\phi_i - n_2 \sin\phi_t}{n_1 \sin\phi_i + n_2 \sin\phi_t} \quad , \qquad r_p = \frac{n_1 \sin\phi_t - n_2 \sin\phi_i}{n_1 \sin\phi_t + n_2 \sin\phi_i}$$

$$n = (1-\delta) - i\kappa = 1 - 2.7019 \times 10^{10} \frac{\rho\lambda^2}{a_w} (f_1 + if_2)$$

Fig. 1

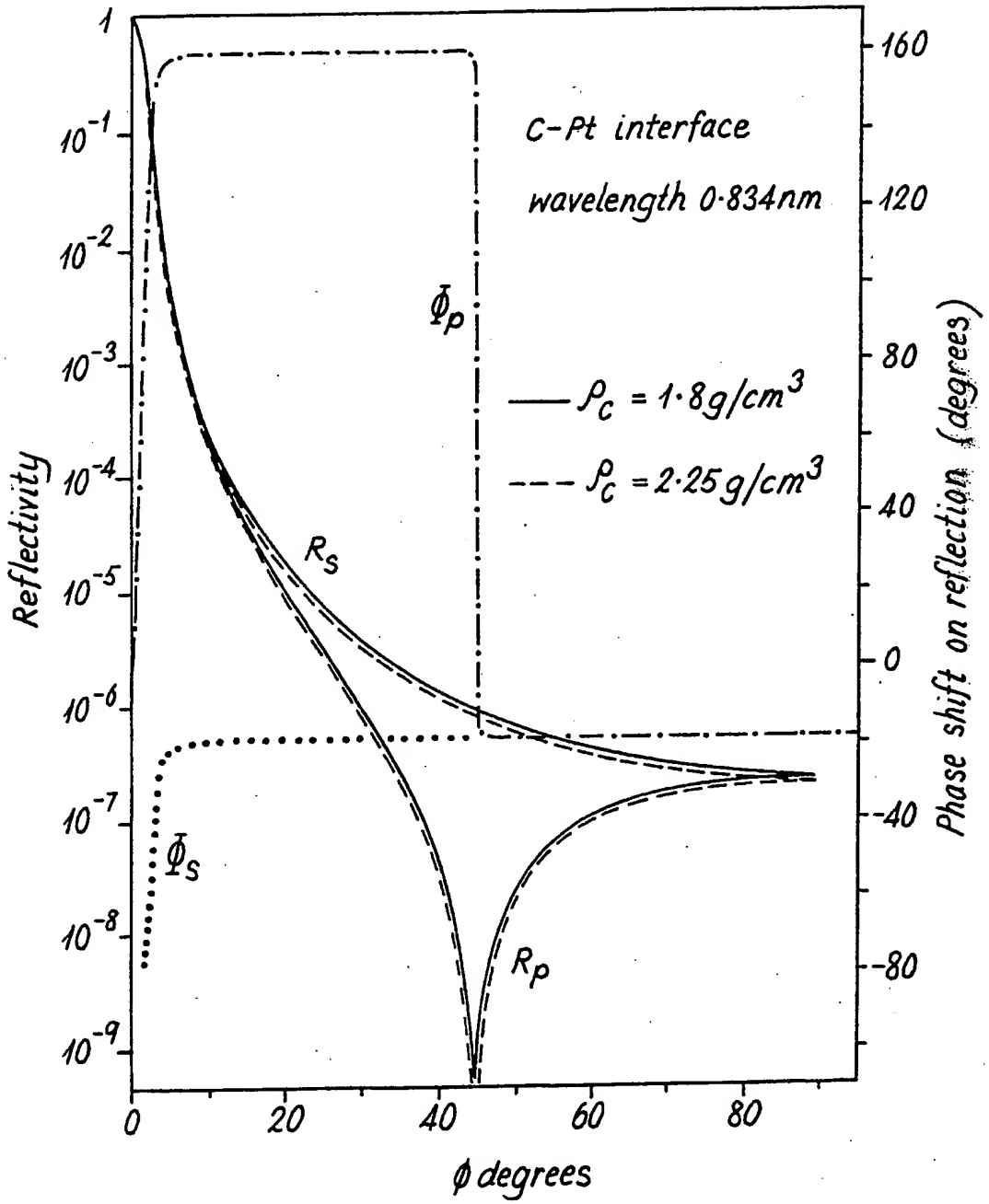

C-Pt interface
wavelength 0·834nm
$\rho_c = 1{\cdot}8 g/cm^3$
$\rho_c = 2{\cdot}25 g/cm^3$
Φ_p
Φ_s
R_s
R_p
Reflectivity
Phase shift on reflection (degrees)
ϕ degrees
1
10^{-1}
10^{-2}
10^{-3}
10^{-4}
10^{-5}
10^{-6}
10^{-7}
10^{-8}
10^{-9}
160
120
80
40
0
-40
-80
0
20
40
60
80

Fig. 2

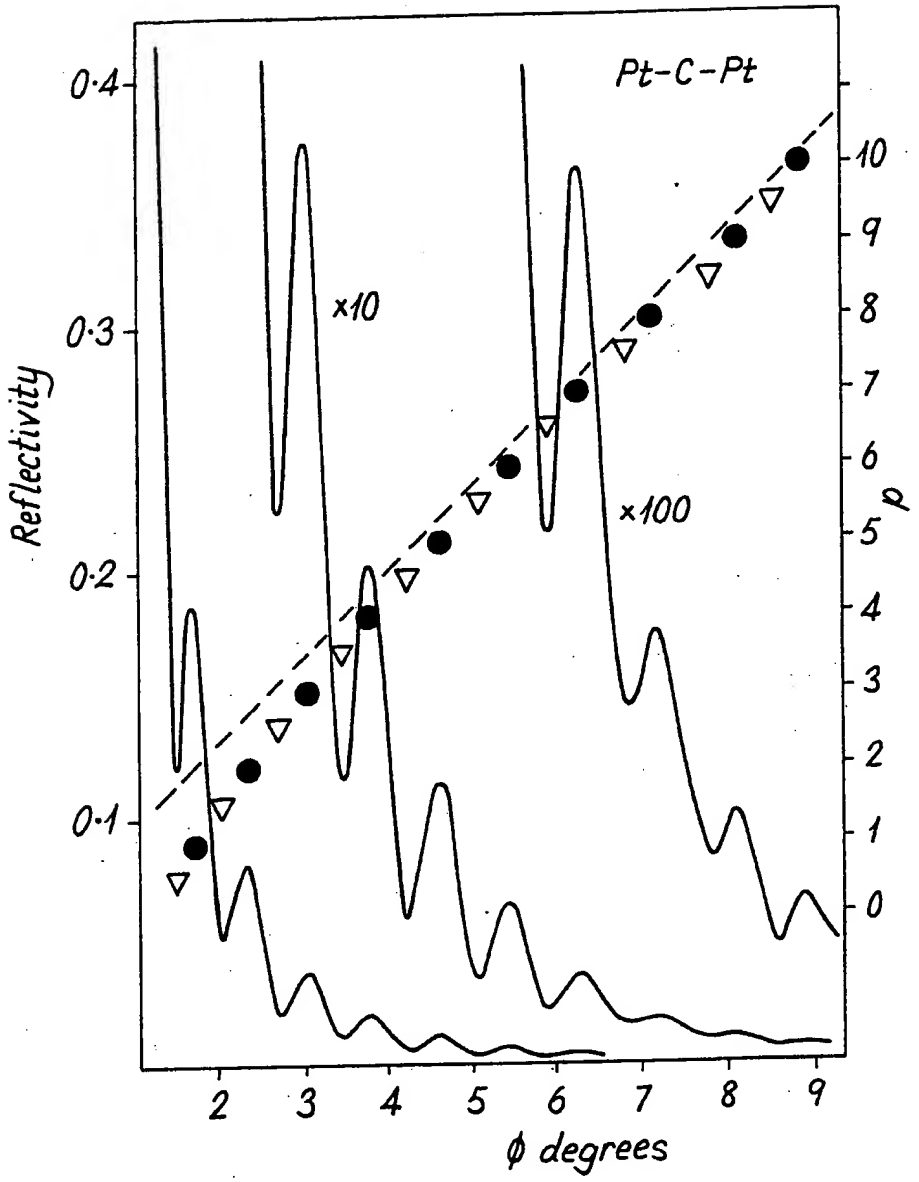

Pt-C-Pt
×10
×100
Reflectivity
0·4
0·3
0·2
0·1
2
3
4
5
6
7
8
9
ϕ degrees
10
9
8
7
6
5
4
3
2
1
0
ρ

Fig. 3

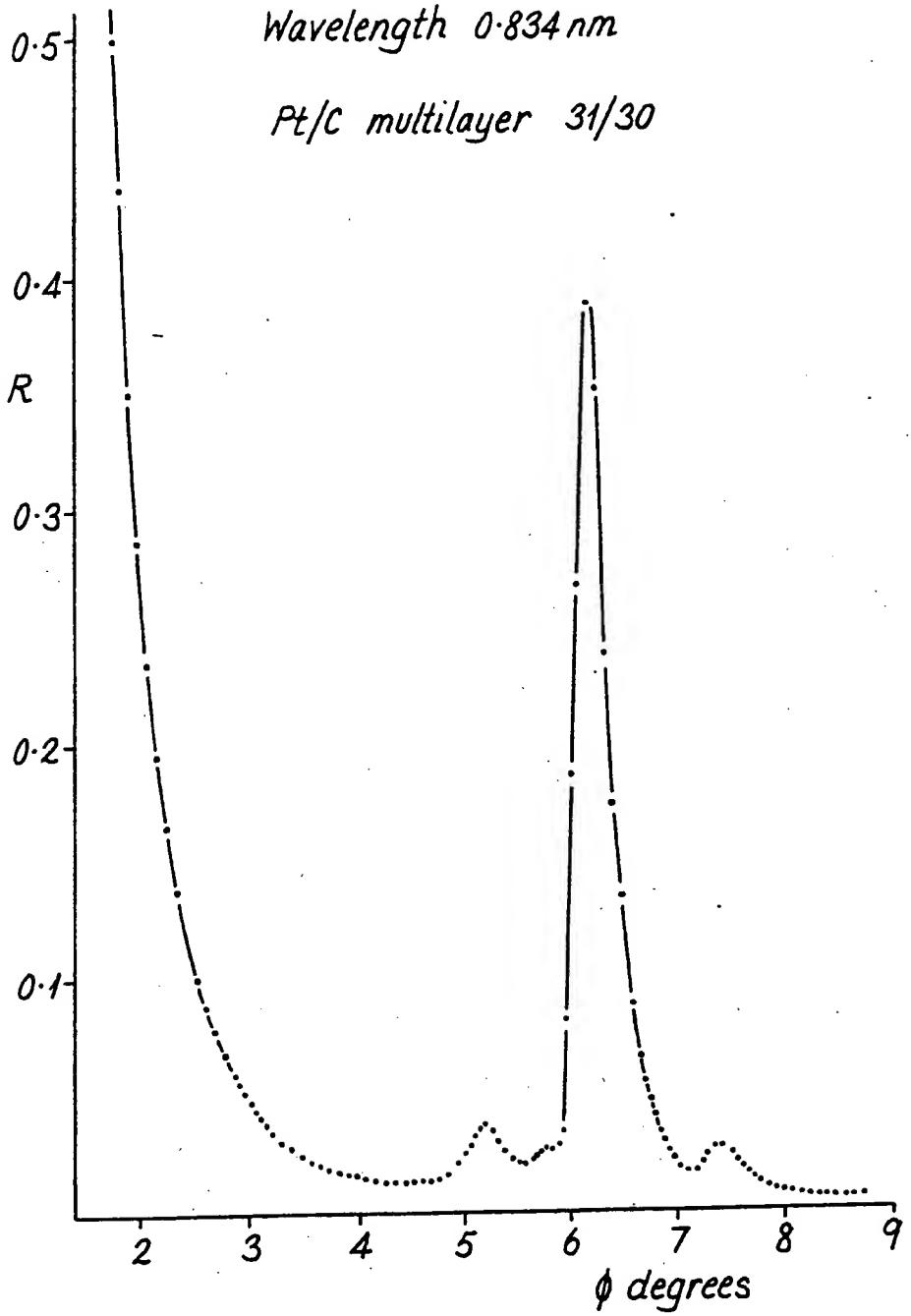

Wavelength 0·834 nm
Pt/C multilayer 31/30
0·5
0·4
R
0·3
0·2
0·1
2
3
4
5
6
7
8
9
ϕ degrees

Fig. 4

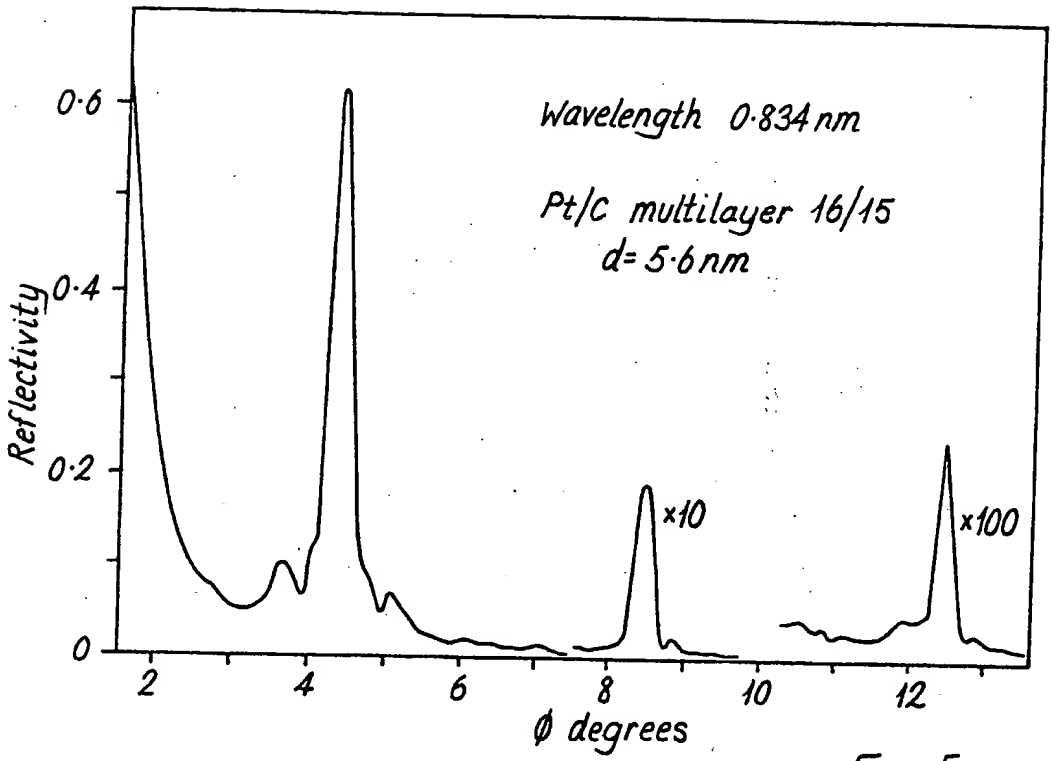

Wavelength 0·834 nm
Pt/C multilayer 16/15
d= 5·6 nm
Reflectivity
0·6
0·4
0·2
0
x10
x100
2
4
6
8
10
12
ø degrees

Fig.5

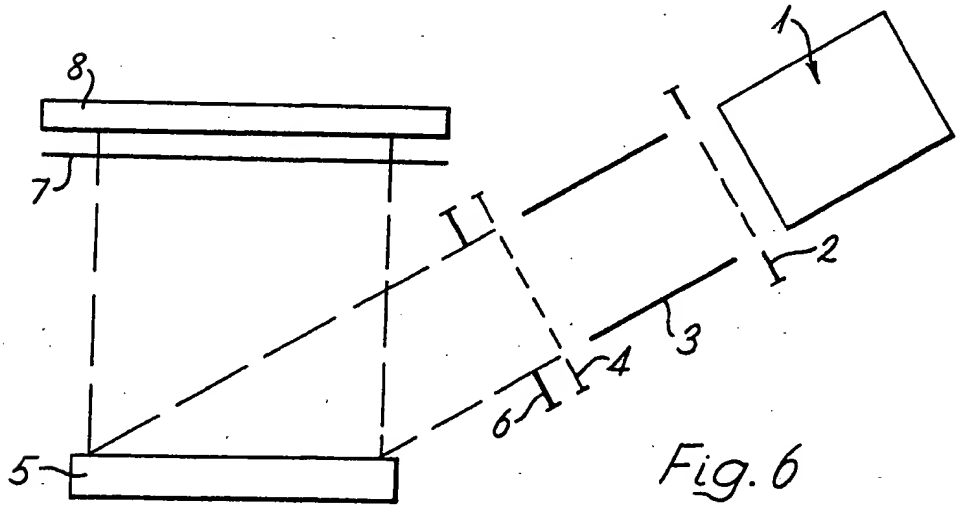

1
2
3
4
5
6
7
8

Fig. 6

INTERNATIONAL SEARCH REPORT

International Application No PCT/GB 87/00891

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) [6]

According to International Patent Classification (IPC) or to both National Classification and IPC

IPC[4]: C 23 C 14/46; C 30 B 29/60

II. FIELDS SEARCHED

Minimum Documentation Searched [7]

Classification System	Classification Symbols
IPC[4]	C 23 C; C 30 B; H 01 L; G 02 B

Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched [8]

III. DOCUMENTS CONSIDERED TO BE RELEVANT [9]

Category [10]	Citation of Document, [11] with indication, where appropriate, of the relevant passages [12]	Relevant to Claim No. [13]
X	US, A, 4261771 (DINGLE et al.) 14 April 1981 see claim 1 --	7,8
A	US, A, 4142958 (WEI et al.) 6 March 1979 see abstract; figure 1 --	1,2,12
A	Patent Abstracts of Japan, volume 9, no. 237 (C-305)(1960), 24 September 1985, & JP, A, 6096761 (TOYODA CHUO KENKYUSHO K.K.) 30 May 1985 see the whole abstract --	1,12
A	Applied Physics Letters, volume 49, no. 15, 13 October 1986, American Institute of Physics, (New York, US), K.S. Seo et al.: "Interdiffusion and wavelength modification in $In_{0.53}Ga_{0.47}As/In_{0.52}Al_{0.48}As$ quantum wells by lamp annealing", pages 966-968 see page 966, paragraphs 1,2 --	3-5,11

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* Special categories of cited documents: [10]

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IV. CERTIFICATION

Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report
17th March 1988	18 APR 1988
International Searching Authority	**Signature of Authorized Officer**
EUROPEAN PATENT OFFICE	P.C.G. VAN DER PUTTEN

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III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)

Category *	Citation of Document, with indication, where appropriate, of the relevant passages	Relevant to Claim No
A	Journal of the Physical Society of Japan, volume 55, no. 5, May 1986, K. Shiraishi et al.: "Electronic structure of metal-semiconductor superlattice", pages 1716-1727 see page 1716, "Introduction"	9,10

ANNEX TO THE INTERNATIONAL SEARCH REPORT ON INTERNATIONAL PATENT APPLICATION NO. GB 8700891 SA 19890

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The members are as contained in the European Patent Office EDP file on 06/04/88
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Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US-A- 4261771	14-04-81	None	
US-A- 4142958	06-03-79	FR-A,B 2422729	09-11-79
		GB-A,B 2020701	21-11-79
		DE-A,C 2902848	18-10-79
		JP-A- 54138878	27-10-79
		CA-A- 1104093	30-06-81